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(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

George C. Marshall Space Flight Center
National Aeronautics & Space Administration
Huntsville, Alabama

IIT RESEARCH INSTITUTE

Report No. IITRI-U6002-31
(Triannual Report)

# DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

Contract No. NAS8-5379
IITRI Project U6002


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## FOREWORD

This is Report No. IITRI-U6002-31 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." The report covers the period from May 20 through September 20, 1965. Previous Triannual Reports were issued on October 25, 1963, March 5, 1964, July 20, 1964, December 21, 1964, February 23, 1965, and July 20, 1965.

Because of a divisional re-organization and accompanying administrative change, the IITRI project number designating this program has been changed. Two new divisions have been formed from what was originally the Chemistry Division - Applied Chemistry (Division C) and Chemical Sciences (Division U). Project administration and technical organization, however, are not affected. Projects assigned to sections within the Chemical Sciences Division have accordingly been redesignated. Since the Polymer Section, which administers this program, is in Division U, the project C6014 has become project U6002.

Major contributors to the program include Gene A. Zerlaut, Project Leader; John E. Gilligan, general consultation; Dr. G. A. Rubin and R. F. Firestone, inorganic coatings; Warren Jamison, W. C. Courtney and C. A. Erdman, silicone irradiations and mass spectrometry; R. Serway, Dr. G. Noble and V. Raziunas, electron spin resonance studies; Douglas G. Vance, silicone paint preparation and space chamber tests; and N. D. Bennett, reflectance measurements. Dr. T. H. Meltzer, Manager of Polymer Research, provides administrative supervision. The work reported herein was performed under the technical direction of the Research Projects Laboratory of the George C. Marshall Space Flight Center with Mr. Daniel W. Gates acting as Project Manager.

Data are recorded in IITRI Logbooks C13423, C13736, C13802, and C14176.

Respectfully submitted,

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2383


## ABSTRACT

## DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

This report describes studies aimed at the development of stable thermal-control coatings with the lowest possible ratio of solar absorptance to infrared emittance. The work is currently proceeding in two major directions: (1) studies of inorganic pigments and (2) ultraviolet photolysis studies of methyl silicone polymers.

Accomplishments during the report period included: (1) The observation that porcelain enamels, even those opacified with "unstable" antimony oxide, have exceptional stability. This fact emphasizes the importance of examining the influence on stability of surface states. (2) Doping of zinc oxide with 0.1 and 0.01% lithium improves the stability of zinc oxide powders at little cost to the initial optical properties. (3) Moisture appears to have little effect on the stability of S-13 paint; an S-13 specimen prepared under anhydrous conditions, however, possessed the lowest solar absorptance of any S-13 film prepared thus far, 0.15 for a 5-mil film. (4) A B-staged Owens-Illinois Type 650 resin that was pigmented with SP 500 zinc oxide exhibited improved physical properties and a solar absorptance increase of only 0.002 after an exposure of 1700 equivalent sun-hours.

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## DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

### I. INTRODUCTION

The general requirement under this contract is for development of thermal-control surface coatings with a very low but stable ratio of solar absorptance ($\alpha$) to infrared emittance ($\epsilon_H$). The work is currently proceeding in two major directions: (1) studies of inorganic pigments and (2) ultraviolet photolysis studies of methyl silicone polymers. Secondary efforts involve (1) synthesis of methyl silicone polymers in support of the photolysis investigations, (2) investigations of inorganic pigment binders, and (3) general screening of zinc oxide-pigmented silicones and potentially useful polymers.

The studies of inorganic pigments involve screening and evaluation of materials parameters that affect pigment stability. These studies are aimed at finding or preparing stable pigments that are potentially useful in formulating coatings with a very low solar absorptance. Emphasis has been placed on the preparation parameters affecting degradation.

The ultraviolet photolysis of methyl silicone polymers involve electron spin resonance and mass spectrometry investigations of carefully prepared methyl and methyl-aromatic silicones irradiated in a vacuum at the following temperatures: liquid nitrogen, ambient (60°C), and elevated (150°C). Work during this report period has involved photolysis studies on General Electric's RTV-602 and Owens-Illinois Type 650 Glass Resin polymer. These studies are aimed at explaining the mechanism of ultraviolet degradation of methyl silicone polymers and will hopefully lead to the synthesis of more stable methyl silicone systems.

## II. INORGANIC COATINGS

### A. Introduction

The studies of inorganic coatings reported here have followed the course outlined in the last Triannual Report, IITRI-C6014-26, July 20, 1965. Screening studies and studies of coatings have been continued, but greater emphasis has been placed on studies and the preparation parameters affecting the degradation of white pigments. The white pigments which have been studied have been dielectrics, i.e., those materials with a band gap energy greater than 6 eV, which do not absorb in the near ultraviolet, since only these materials offer a chance of obtaining a pigment with greater reflectance than zinc oxide.

### B. Results of Solar Simulation Tests

The results of the solar simulation tests conducted during this period are summarized in Table 1. Pertinent data on the pigment specimens are contained in Table 2. The majority of materials were studied as powder compacts and no binder was used. This method of mounting avoids binder effects which can often have a major influence on the observed degradation.

Potassium silicate-bonded coatings with four different zinc oxide pigments, which had been prepared over a year ago and stored under normal laboratory conditions, were irradiated in test V65 as specimens 7170 and 7173. The data show that the degradation resistance of these coatings is not impared by

Table 1

| Test | Specimen | Pigment | Binder | Remarks | Solar Factor | Exposure ESH | Solar Absorptance | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $\alpha_1$ | $\alpha_2$ | $\alpha$ | $\Delta\alpha$ |
| V64 | 7151 | CaO | None | Uncalcined | 0 | 0 | .024 | .075 | .099 | |
| | | | | | 10 | 2367 | .272 | .136 | .408 | +.309 |
| | 7158 | $ZrO_2$ | None | Calcined 2000°F | 0 | 0 | .051 | .031 | .082 | |
| | | | | | 10 | 2367 | .248 | .079 | .327 | +.245 |
| | 7164 | CaO | None | Calcined 2000°F | 0 | 0 | .019 | .073 | .092 | |
| | | | | | 10 | 2367 | .227 | .096 | .323 | +.231 |
| | 7169 | $TiO_2$ | Borosilicate | Porcelain enamel | 0 | 0 | .136 | .106 | .242 | |
| | | (rutile) | glass | on aluminum | 10 | 2367 | .148 | .110 | .258 | +.016 |
| V65 | 7170 | ZnO | PS7(PBR 4.3) | | 0 | 0 | .097 | .049 | .146 | |
| | | (55LO) | | | 10 | 2150 | .098 | .045 | .143 | -.003 |
| | 7171 | ZnO | PS7(PBR 4.3) | | 0 | 0 | .106 | .070 | .176 | |
| | | (XX254) | | | 10 | 2150 | .111 | .064 | .180 | +.004 |
| | 7172 | ZnO | PS7(PBR 4.3) | | 0 | 0 | .150 | .090 | .240 | |
| | | (EP-730) | | | 10 | 2150 | .101 | .091 | .252 | +.012 |
| | 7173 | ZnO | PS7(PBR 4.3) | Z93 | 0 | 0 | .083 | .069 | .152 | |
| | | (SP500) | | | 10 | 2150 | .088 | .048 | .136 | -.016 |
| | 7174 | $ZrO_2$ | Borosilicate | Porcelain enamel | 0 | 0 | .175 | .234 | .409 | |
| | | | glass | on iron | 10 | 2150 | .158 | .237 | .395 | -.014 |
| | 7175 | $Sb_2O_3$ | Borosilicate | Porcelain enamel | 0 | 0 | .163 | .192 | .355 | |
| | | | glass | on iron | 10 | 2150 | .181 | .205 | .385 | +.030 |
| | 7176 | $TiO_2$ | Borosilicate | Porcelain enamel | 0 | 0 | .141 | .111 | .252 | |
| | | (rutile) | glass | on iron | 10 | 2150 | .148 | .112 | .260 | +.008 |
| V67 | 7177 | ZnO | None | Undoped | 0 | 0 | .084 | .037 | .121 | |
| | | | | | 10 | 1760 | .092 | .042 | .134 | +.013 |
| | 7178 | $ZrO_2$ | None | Flourescent | 0 | 0 | .071 | .042 | .113 | |
| | | | | grade | 10 | 1760 | .104 | .045 | .149 | +.036 |
| | 7179 | ZnO | None | SP500 1.5 $\mu$ | 0 | 0 | .091 | .017 | .108 | |
| | | | | | 10 | 1760 | .094 | .024 | .118 | +.010 |
| | 7180 | ZnO | None | .01% Li-Doped | 0 | 0 | .090 | .038 | .128 | |
| | | | | | 10 | 1760 | .094 | .041 | .134 | +.004 |
| | 7181 | ZnO | None | .1% Li-Doped | 0 | 0 | .087 | .043 | .130 | |
| | | | | | 10 | 1760 | .093 | .042 | .135 | +.005 |
| V69 | 7182 | $3Al_2O_3\cdot$ | None | Fused grain | 0 | 0 | .144 | .140 | .284 | |
| | | $2SiO_2$ | | | 10 | 200 | .203 | .147 | .350 | +.066 |
| | 7183 | $Al_2O_3$ | None | Fused grain | 0 | 0 | .038 | .041 | .071 | |
| | | | | | 10 | 200 | .189 | .060 | .249 | +.178 |
| | 7184 | $ZrO_2$ | None | Fused grain | 0 | 0 | .176 | .183 | .359 | |
| | | | | | 10 | 200 | .196 | .189 | .385 | +.026 |
| | 7185 | $Al_2O_3$ | None | Calcined 1650°F | 0 | 0 | .019 | .080 | .099 | |
| | | | | | 10 | 200 | .340 | .156 | .496 | +.397 |
| | 7186 | $Al_2O_3$ | None | Calcined 1100°F | 0 | 0 | .021 | .091 | .112 | |
| | | | | | 10 | 200 | .421 | .222 | .643 | +.531 |
| V70 | 7187 | $SnO_2$ | None | Uncalcined | 0 | 0 | .097 | .043 | .140 | |
| | | | | | 10 | 300 | .203 | .152 | .353 | +.213 |
| | 7188 | $SnO_2$ | None | Calcined 1100°F | 0 | 0 | .102 | .052 | .154 | |
| | | | | | 10 | 300 | .246 | .213 | .459 | +.305 |
| | 7189 | $MoO_3$ | None | Single crystal | 0 | 0 | .199 | .191 | .390 | |
| | | | | powder | 10 | 300 | .437 | .442 | .879 | +.489 |
| | 7190 | $Ta_2O_5$ | None | Calcined 1500°F | 0 | 0 | .051 | .018 | .069 | |
| | | | | | 10 | 300 | .130 | .033 | .164 | +.095 |
| | 7191 | $Al_2O_3$ | None | Fused grain | 0 | 0 | .088 | .066 | .154 | |
| | | | | | 10 | 300 | .133 | .064 | .197 | +.043 |

Table 2

PIGMENT CHARACTERISTICS

| Specimen No. | Composition | Purity | Average Particle Size | Method of Mfg. | Manufacturer | Mfg. type No or Grade | Remarks |
|---|---|---|---|---|---|---|---|
| 7151<br>7164 | CaO | 99.9% | | Calcination | Whittaker Clark & Daniels | C.P. | |
| 7158 | $ZrO_2$ | 99.9% | | Calcination | Titanium Alloy Mfg. Company | High purity | |
| 7169 | $TiO_2$ (rutile) | | | Precipitation from molten glass | Chicago Vitreous Co. | | Porcelain enamel on aluminum |
| 7170 | ZnO | 99.2% | .40 μ | Calcination | American Zinc Co. | 55LO | |
| 7171 | ZnO | 99.6% | 1.5 μ | Calcination | N. J. Zinc Co. | XX254 | |
| 7172 | ZnO | 99.5% | 5.4 μ | Calcination | Eagle-Pitcher Co. | EP730 | |
| 7173 | ZnO | 99.9% | .30 μ | Calcination | N. J. Zinc Co. | SP500 | |
| 7174<br>7175<br>7176 | $ZrO_2$<br>$Sb_2O_3$<br>$TiO_2$(rutile) | | | Precipitation from molten glass | Chicago Vitreous Co. | | Porcelain enamel on iron |
| 7177<br>7180<br>7181 | ZnO<br>ZnO .01% Li<br>ZnO .1% Li | 99.5% | | Coprecipitation and calcination | N. J. Zinc Co. | USP-12 | |
| 7178 | $ZrO_2$ | 99% | | Calcination | Titanium Alloy Mfg. Company | Flourescent grade | |
| 7179 | ZnO | 99.9% | 1.5 μ | Calcination | Titanium Alloy Mfg. Company | SP500 | Reheated |
| 7182<br>7183<br>7184<br>7191 | 3 $Al_2O_3$-2$SiO_2$<br>$Al_2O_3$<br>$ZrO_2$<br>$Al_2O_3$ | 95%<br>95%<br>98%<br>99.6% | 44 μ<br>3.0 μ<br>7.5 μ<br>7.5 μ | Fusion | Norton Company | Mullnorite<br>Alundum 38<br>Zirnorite<br>38900 | <br>"Flour"<br><br>Acid washed |
| 7185<br>7186 | $Al_2O_3$ | 99% | | Calcination | Alcoa | C-33 | |
| 7187<br>7188 | $SnO_2$ | 99% | | Calcination | M & T Company | Prime metal grade | |
| 7189 | $MoO_2$ | 99% | | Vapor deposition | IITRI | | |
| 7190 | $Ta_2O_5$ | | | Calcination | Titanium Alloy Mfg. Company | High purity | |

storage. Of the four coatings, the standard Z93 was affected least by ultraviolet irradiation in vacuum. The effect of the binder may be seen when specimen 7173 (where SP500 zinc oxide is used with PS7 potassium silicate binder) is compared with specimen 7179 (where SP500 is binderless in a powder compact). (The effect of different grain size can be ignored since comparison with previous tests shows that it has little effect). The pigment alone has a lower initial solar absorptance, $\alpha$, but also experiences greater degradation, $\Delta\alpha$. The negative $\Delta\alpha$ for the paint (Z93) is attributed to the reflectance increase in the $\alpha_2$-region as a result of loss of water by the silicate vehicle (ref. 1).

The effect of binder, which in this case is a borosilicate glass matrix, is greatly emphasized by the ultraviolet/vacuum irradiation of porcelain enamel specimens, 7169, 7174, 7175, and 7176. In every case, the degradation of the pigment in the enamel is much less than of the pigment alone or in a silicate binder. Even an easily degradable pigment such as antimony oxide becomes moderately stable when incorporated in the enamel! These specimens were cut from standard commercial test panels which were coated with enamel for minimum acceptable opacity. We believe that specimens could be prepared which would show a much higher reflectance by applying thicker coatings possessing greater amounts of pigment opacifiers.

Experiments on heat treatment of pigments suggest that calcination has a beneficial effect on dielectric pigments such as lime (specimens 7151 and 7164) and alumina (specimens 7185 and 7186); however, a deleterious effect was noted for stannic oxide, a semiconductor pigment (specimens 7187 and 7188). If it is true that degradation is due to surface states and that lowering the surface area (and hence the surface energy) of a pigment improves resistance to degradation, then the behavior of stannic oxide is irregular, since heat treatment is known to lower its surface area. However, it also may have changed its stoichiometry. Cox (ref. 2) has recently studied the effect on stability of particle size and concluded that larger particles exhibit less degradation at equal volume concentrations. Of course this may be due not only to the lower surface energy, but also to the significantly lessened ultraviolet pathlength (random) exhibited by paints with large compared to small pigment-particle size distributions.

Fused grain has the lowest surface area of any calcined powder of equivalent grain size and would be expected to have good degradation resistance. Four specimens, 7182, 7183, 7184 and 7191 of fused grain of various compositions were irradiated and the former expectation was not borne out. The fused grain was not superior to <u>all</u> calcined materials of the same composition in terms of degradation resistance. However, the factor of purity may be involved: the fused grains are of only nominal purity (about 98%) while most of the calcined materials tested were quite pure (greater than 99.9%).

An attempt was made to obtain samples of very pure (less than 100 ppm total impurities) white materials for testing. Prof. Ivan Cutler of the University of Utah generously donated some samples, but these were too small to test. Samples ordered three months ago from a commercial source (Cominco) to be made from zone-refined metals have not arrived.

As mentioned in the previous Triannual Report, IITRI-C6014-26, it is known that the Fermi level of zinc oxide can be lowered by substitutional doping with lithium. It has been suggested that, while the overall reflectance might be lowered slightly by doping, subsequent ultraviolet-induced degradation might be reduced or eliminated. To test this hypothesis, samples of zinc oxide with two levels of lithium doping were obtained from the New Jersey Zinc Company and evaluated (specimens 7177, 7179, and 7180). As hoped for, the overall reflectance was lowered only slightly while the stability of the zinc oxide was improved.

Molybdic oxide (specimen 7189) was selected for testing on the basis of its band gap, its position in the Periodic Table, and its atomic structure. It proved to be extremely unstable and high vacuum alone was sufficient to cause a marked decrease in its reflectance.

## C. Discussion

The results of these tests are strongly suggestive of the considerable influence of surface conditions on degradation resistance of pigment powders. Other factors such as purity and composition are also operational. Many of the results cannot be explained at this time and it is hoped that work will elucidate the factors involved.

Experimental and theoretical considerations indicate that the ultraviolet degradation of oxide pigments is caused, partially or totally, by oxygen - vacancy and interstitial cation states which form donor levels within the visible spectrum, the oxygen vacancies probably being more detrimental (E = 0.8 eV) than the interstitial metal ions (E = 0.05 eV). Since the extent of degradation seems to be inversely proportional to the grain size of the pigment-crystals and also to the oxygen partial pressure, independently, the oxygen vacancies seem to be located originally at the surface of the crystallites -- the depth of the degraded zone depending upon the diffusion of the vacancies into the bulk of the crystal. This, then, seems to support the hypothesis according to which:

a. Holes are generated by ultraviolet-radiation (together with free-electrons, of course).

b. The holes move to the surface of the crystallites, attracted by the negative surface charge (Fermi level in n-type conductors like ZnO, which is probably above the surface-state levels).

c. At the surface, the holes partially neutralize the chemically absorbed oxygen ($O^{--} \rightarrow O^{-}$), releasing oxygen from the surface.

d. The so-created oxygen vacancies diffuse into the crystallites, in which electrons become trapped causing optical absorption.

The reader is referred to two IITRI reports for more detailed discussions of the pigment-photolysis problem (ref. 3 and 4).

On the basis of this hypothesis, the following suggestions are made to help reduce degradation effects:

a. Use of n-type conductors,

b. Grain size as large as permissable and still maintain high reflectance.

c. Use of fused or semifused crystallites or a mixture of semifused and calcined material.

For instance, by treating the pigment-powder with an oxidizing torch and applying a very high temperature over an extremely short time, it should be possible to obtain crystallites with a fused surface. The advantage is less surface state/$cm^2$ compared to "calcined surfaces". This means much less chemically absorbed oxygen which, in turn, reduces the possibility for surface oxygen-vacancy generation. Since the density of the fused material probably is higher than that of the nonfused material, this would also incorporate a higher reflectance (increase of refractive index).

## D. Future Work

Some of the suggestions outlined in the Discussion have already been partially carried out and were discussed in the foregoing pages. The results have been a tentative confirmation of the theory that surface states are responsible for degradation. A series of experiments have been planned on this basis using high surface area alumina and zirconia as the starting materials and gradually reducing its surface area, and thereby surface energy, by calcination at increasingly higher temperatures until incipient fusion occurrs. Thus, a series of data will be obtained which should clearly show the influence of surface area on degradation resistance.

Screening tests will be continued on white materials which might be suitable pigments for coatings on the basis of their absorptance and index of refraction.

## III. METHYL SILICONE PAINTS AND MISCELLANEOUS SPECIMENS

### A. Space-Simulation Test V-65

Six silicone paints were evaluated in test V-65. The results of this space-simulation test are presented in Table 3. Specimen 5154 was prepared in order to evaluate Dow Corning's Q-93-024 proprietary RTV methyl silicone polymer. The $\Delta\alpha$ of 0.045 after 2150 ESH exposure indicates that the Q93-024 is not as stable as the S-13 formulations based on RTV-602 which were irradiated in the same test. The S-13 specimens, which were prepared in conjunction with another program,* underwent solar absorptance increases of 0.024 to 0.035 in this space-simulation test. The S-13 specimens were prepared at the standard catalyst concentration of 0.76% based on RTV-602; specimens irradiated at a lower catalyst concentration, e.g., 0.4% of resin weight, usually degrade only 0.02 in about 2000 ESH.

The rutile-pigmented RTV-602 paint underwent an increase in solar absorptance of about 0.05 (compared to a $\Delta\alpha$ of 0.025 when dispersed in Owens-Illinois Type 650 Glass Resin). The rutile is Cabot's Flame-Process titania and it is the most stable titanium dioxide which we have examined. These rutile paints exhibit about twice the damage exhibited by SP500 paints prepared from the same polymers.

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*Contract NAS8-11133, George C. Marshall Space Flight Center

Table 3

EFFECT OF UV IRRADIATION IN VACUUM ON SEVERAL SILICONE PAINTS (Test V-65)

| Specimen | Pigment | Binder | Remarks | Solar Factor | Exposure ESH | Solar Absorptance $\alpha_1$ | Solar Absorptance $\alpha_2$ | Solar Absorptance $\alpha_s$ | Solar Absorptance $\Delta\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| 5150* | SP500 ZnO | RTV-602 | S-13 | 0 | 0 | .087 | .094 | .181 | |
| | | | PVC = 35% | 10 | 2150 | .108 | .097 | .205 | .024 |
| 5151* | SP500 ZnO | RTV-602 | S-13 | 0 | 0 | .086 | .093 | .179 | |
| | | | PVC = 35% | 10 | 2150 | .119 | .094 | .213 | .034 |
| 5152* | SP500 ZnO | RTV-602 | S-13 | 0 | 0 | .086 | .087 | .173 | |
| | | | PVC = 35% | 10 | 2150 | .113 | .095 | .208 | .035 |
| 5153* | SP500 ZnO | RTV-602 | S-13 | 0 | 0 | .087 | .088 | .175 | |
| | | | PVC = 35% | 10 | 2150 | .112 | .091 | .203 | .028 |
| 5154 | SP500 ZnO | Dow Corning | PVC = 30% | 0 | 0 | .087 | .081 | .168 | |
| | | Q93-024** | Heptane | 10 | 2150 | .129 | .084 | .213 | .045 |
| 5155 | r-$TiO_2$/ | RTV-602 | PVC = 30% | 0 | 0 | .089 | .086 | .175 | |
| | Cabot | | Toluene | 10 | 2150 | .117 | .107 | .224 | .049 |
| 5156 | $\alpha$-$Al_2O_3$ | OI 650 | PVC = 30% | 0 | 0 | .251 | .256 | .507 | |
| | (Lexington) | | No Solvent | 10 | 2150 | .428 | .286 | .714 | .207 |
| 5157 | $\alpha$-$Al_2O_3$ | OI 650 | PVC = 30% | 0 | 0 | .059 | .099 | .158 | |
| | (Alucer MC) | | No Solvent | 10 | 2150 | .085 | .105 | .191 | .032 |
| 5158 | $ZrO_2$ | PS7 Potassi- | PBR = 6.40 | 0 | 0 | .043 | .046 | .089 | |
| | | um silicate | | 10 | 2150 | .128 | .056 | .184 | .095 |

*Prepared for use on contract NAS8-11967

**Used with 10 pph Dow Corning's proprietary catalyst

Because of the fine particle size of the low-defect alumina obtained from Mr. William Campbell of Lexington Laboratories, Inc., this material was prepared as a mull in Owens-Illinois Type 650 Glass Resin. Alucer MC $\alpha$-alumina was used to prepare an otherwise identical paint for comparison purposes. The low-defect alumina suffered severe damage ($\Delta\alpha$ = 0.21) compared to the damage exhibited by the $\alpha$-alumina (5157) obtained from Gulton Industries. The later coating underwent an increase in solar absorptance of only 0.03, which is in complete disagreement with previous results on $\alpha$-alumina coatings (ref. 3).

The zirconia control specimen exhibited a solar absorptance increase of 0.095. This amount of damage is consistent with exposures of approximately 2000 ESH, indicating a valid test in terms of average ultraviolet intensity.

## B. Space-Simulation Test Q-16

Test Q-16 was performed in the Quad-Ion test facility. The nominal ultraviolet intensity was 5 suns and the total exposure was calculated to be 1700 ESH. The results of this test are presented in Table 4.

Specimen 5191 was prepared in order to check the excellent stability of the Alucer MC $\alpha$-alumina paint observed in test V65. The $\Delta\alpha$ of 0.06 made it mandatory that additional specimens be prepared and exposed to ultraviolet radiation in vacuum. Specimens have been included in a space-simulation test currently in progress.

Table 4

EFFECT OF UV IRRADIATION IN VACUUM ON SEVERAL SILICONE FILMS (Test Q-16)

| Specimen | Chamber | Pigment | Binder | Remarks | Solar Factor | Exposure ESH | Solar Absorptance $\alpha_1$ | $\alpha_2$ | $\alpha_s$ | $\Delta\alpha$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 5191 | 2 | $\alpha$-$Al_2O_3$* | OI 650 | PVC = 30% | 0 | 0 | .029 | .059 | .088 | |
| | | | | No solvent | 5 | 1700 | .094 | .056 | .150 | .062 |
| 5192 | 1 | SP500 ZnO | RTV-602 | S-13/Dry | 0 | 0 | .088 | .064 | .152 | |
| | | | | | 5 | 1700 | .090 | .072 | .162 | .010 |
| 5193 | 1 | SP500 ZnO | RTV-602 | S-13/Wet | 0 | 0 | .090 | .084 | .174 | |
| | | | | | 5 | 1700 | .098 | .089 | .187 | .013 |
| 5194 | 1 | SP500 ZnO | OI 650 | B-Staged | 0 | 0 | .087 | .095 | .182 | |
| | | | | Resin | 5 | 1700 | .093 | .092 | .185 | .003 |
| 5195 | 2 | SP500 ZnO | OI 650 | B-Staged | 0 | 0 | .096 | .090 | .186 | |
| | | | | Resin | 5 | 1700 | .097 | .090 | .187 | .001 |
| 5198 | 2 | (Boeing barrier-layer Anodize) | | | 0 | 0 | .099 | .116 | .215 | |
| | | | | | 5 | 1700 | .132 | .123 | .255 | .040 |
| 5199 | 2 | $ZrO_2$ | PS7 | Control | 0 | 0 | .076 | .083 | .159 | |
| | | | | | 5 | 1700 | .153 | .086 | .239 | .080 |
| 5200 | 1 | $ZrO_2$ | PS7 | Control | 0 | 0 | .074 | .079 | .153 | |
| | | | | | 5 | 1700 | .145 | .083 | .228 | .075 |

*Alucer MC $\alpha$-alumina from Gulton Industries

The possible influence of films of moisture on the stability of non-metallic thermal-control coatings has been raised on numerous occasions. Of particular concern has been the possibility of enhancement of photolysis by moisture accumulated prior to or during launch operations. We accordingly prepared specimens of S-13 under both anhydrous and moist conditions.

The "dry" S-13 was prepared by first heating uncatalyzed RTV-602 to 250°F for 1 hour. To the hot RTV-602 was blended an appropriate quantity of moderately hot SP500 ZnO which had been heated to 500°F for 1 hour. The mixture was added to a "dry" ball-mill; when sufficiently cooled, it was milled for 3 hours. Specimens were prepared in a dry atmosphere. The samples were maintained in a dessicator until their reflectances were measured (just prior to insertion in the space-simulation chamber).

The "wet" specimen was prepared by mixing the basic S-13 pigment-polymer slurry with 1% water by weight prior to grinding. The resultant paint was thixotropic and required nearly 24 hrs to cure tack free.

The two specimens, one prepared "wet" (5193) and the other prepared under anhydrous conditions (5192), were irradiated in test Q-16. Both specimens exhibited excellent stability. The $\Delta\alpha$ of specimen 5192 was 0.010; the $\Delta\alpha$ of specimen 5193 was 0.013. The slight difference between the two specimens, though favoring the sample prepared under anhydrous conditions, tends to indicate that any moisture present on insertion into the simulation chamber has little effect on the stability of S-13.

The moisture appears to have caused a higher initial reflectance of S-13. Specimen 5193 was prepared at a thickness of 10 mils and possessed an initial solar absorptance of 0.174; the solar absorptance of specimen 5192, prepared at only 5 mils, was 0.152. The most interesting aspect of this test is the exceptionally low solar absorptance exhibited by the 5-mil specimen of S-13 prepared under anhydrous condition. Additional experiments will be performed to determine the significance of this observation.

A recent lot of Owens-Illinois Type 650 methyl silicone resin was B-staged according to procedures suggested by Owens-Illinois Corporation. This involves slowly heating the resin to 150°F and cooling the resultant material by pouring it into an aluminum-foil tray. The melt is allowed to cool; it is subsequently crushed and re-dissolved in ethanol. An SP500 zinc oxide-paint was prepared from the B-staged material at 30% PVC. When cured by heating at 150°F for several hours, specimens of the B-staged paint exhibited hard, semi-glossy surfaces. Their stability was again exceptional with $\Delta\alpha$'s of 0.001 and 0.003 for two samples (5194 and 5195). The B-staged paint appears to be as stable as paints prepared from the A-staged (stock) polymer.

Specimen 5198 was a sample of the Boeing Company's barrier-layer anodize coating. It exhibited greater stability ($\Delta\alpha$ = 0.04) than anticipated and possessed an initial solar absorptance of 0.22.

The $\Delta\alpha$'s of 0.08 for the two zirconias are indicative of a satisfactory and valid space simulation test; the exposure was determined to be 1700 ESH.

## IV. METHYL SILICONE PHOTOLYSIS

### A. Introduction

The ultimate objective of this portion of the program is the synthesis of silicone polymers that are totally resistant to solar radiation. The immediate objectives are (1) to determine the inherent stability of the basic silicone structure, (2) to determine the mechanism of ultraviolet-degradation processes, (3) to assess the influence of various side-chain or substituent groups, and (4) to assess the influence of contamination on the photolytic processes and to identify those contaminants which promote or otherwise affect polymer degradation.

Ultraviolet photolyses of the silicone polymers are being followed by (1) ultraviolet (differential) absorption spectroscopy, (2) mass spectrometry and (3) electron-spin-resonance spectroscopy.

Twelve polymer specimens have been irradiated with ultraviolet in vacuum since the inception of this phase of the project. The pertinent information concerning these experiments is tabulated in Table 5.

The mass spectra data for tests LP1, LP2 and SP-1 and the electron spin resonance spectra for SP-1 were presented in the last Triannual Report, IITRI-C6014-26. Mass spectra determinations were made on all tests except SP-1B, which was an electron spin resonance (ESR) check on test SP-1.

The mass spectra data for SP-4, SP-5 and SP-6 have been

Table 5

PERTINENT DATA ON METHYL SILICONE PHOTOLYSIS EXPERIMENTS

| Test No. | Material | Solid (S) or Liquid (L) | Remarks | ESR Spectra |
|---|---|---|---|---|
| LP-1 | Linear Polydimethylsiloxane | L | p. 30, IITRI-C6014-26 | Negative |
| LP-2 | Linear Polydimethylsiloxane | L | p. 31, IITRI-C6014-26 | Negative |
| SP-1 | Crosslinked ($O_2$) Polymethylsiloxane | S | pp. 24&34, IITRI-C6014-26 | Positive |
| SP-1B | Crosslinked ($O_2$) Polymethylsiloxane | S | Mass Spectra not obtained | Positive |
| LP-4 | RTV-602 Polymethylsiloxane | L | Mass Spectra in Table 6 | Positive |
| SP-2 | Owens-Illinois Type 650 Resin | S | Mass Spectra in Table 7 | Positive |
| SP-3 | RTV-602/0.4% SRC-05 Catalyst | S | Mass Spectra in Table 8 | Positive |
| SP-4 | Owens-Illinois Type 650 Resin | S | Spectra not tabulated | Negative |
| SP-5 | RTV-602/0.4% SRC-05 Catalyst | S | Spectra not tabulated | Negative |
| SP-6 | RTV-602/0.4% SRC-05 Catalyst | S | Spectra not tabulated | Negative |

normalized and tabulated, but have not been analyzed. These data will be presented in the next Triannual Report. Of major significance is the lack of observed ESR spectra for these specimens, a result which will be discussed in a later section.

## B. Mass Spectrometry of Photolyzed Polymer

The mass spectra data, normalized to the nitrogen peak (28 m/e), are presented for specimens LP-4, SP-2, SP-3 and SP-4 in Tables 6 through 9, respectively.

The mass spectra data for LP-4 are presented in Table 6. An increase in hydrogen was observed after completion of ultraviolet irradiation when the gas from the warm polymer was bled into the mass spectrometer. (The apparatus is described in the last Triannual Report, IITRI-C6014-26). The hydrogen content decreased from a relative peak height of 140 prior to irradiation to approximately 50 during irradiation; the peak height increased when the AH-6 lamp was turned off, however. The methane content (14, 15 and 16 m/e) decreased during radiation with no subsequent change after irradiation. The water content (18 m/e) decreased during the irradiation.

The Owens-Illinois Type 650 methyl silicone resin was irradiated in test SP-2 and the data is presented in Table 7. An increase in the hydrogen peak was observed as a result of irradiation of the $LN_2$-cooled polymer. Little difference was noted in the hydrogen peak when the irradiated polymer was warmed after the ultraviolet source was turned off. Of greatest

Table 6

SUMMARY DATA OF TEST LP-4 (RTV-602 UNCATALYZED)

| m/e | Probable Gas Species | Warm Polymer Background | Polymer under $LN_2$ | Polymer under UV + $LN_2$ | Polymer under UV + $LN_2$ | Polymer under $LN_2$ only | Warm Polymer Gas Bleed |
|---|---|---|---|---|---|---|---|
| 2 | $H^+$ | 140 | 49 | 50 | 45.5 | 114 | 366 |
| 12 | $C^+$ | 6 | 4.6 | 4.6 | 3.6 | 1.4 | 1.7 |
| 13 | $CH^+$ | 0.6 | 0.5 | 0.3 | Trace | 0.3 | Trace |
| 14 | $CH_2^+$,$N^+$ | 6 | 8.9 | 8.9 | 9.1 | 8.5 | 9.4 |
| 15 | $CH_3^+$ | 5 | 3.3 | 2.4 | 1.6 | 3.8 | 3.1 |
| 16 | $CH_4^+$, $O^+$ | 10.6 | 6.8 | 5.5 | 4.6 | 0.5 | 4.7 |
| 17 | $OH^+$,$CH_5^+$ | 22 | 8.6 | 5.6 | 4.6 | 3.1 | 3.1 |
| 18 | $H_2O^+$ | 109 | 26.4 | 16.1 | 13.5 | 10 | 11.3 |
| 25 | $C_2H^+$ | Trace | Trace | Trace | Trace | | |
| 26 | $C_2H_2^+$ | 1.1 | 0.9 | 0.7 | 0.5 | 0.4 | 0.6 |
| 27 | $C_2H_3^+$ | 1.9 | 1.1 | 1.1 | 0.7 | 0.7 | 1.2 |
| 28 | $C_2H_4^+$,$CO^+$,$N_2^+$ | 100 | 100 | 100 | 100 | 100 | 100 |
| 29 | $C_2H_5^+$ | 2.2 | 1.4 | 1.1 | 1.2 | 1.3 | 2.2 |
| 30 | $C_2H_6^+$ | 0.6 | Trace | 0.3 | 0.2 | 0.2 | Trace |
| 32 | $O_2^+$ | 1.8 | 1.7 | 1.6 | 1.8 | 0.5 | Trace |
| 39 | $C_3H_3^+$ | 0.2 | 0.2 | Trace | Trace | Trace | Trace |
| 40 | $C_2O^+$,$A^+$ | 0.2 | 0.2 | 0.5 | 0.5 | 0.9 | 0.9 |
| 44 | $CO_2^+$ | 4.3 | 4.3 | 4.8 | 4.6 | 1.7 | 1.3 |

Table 7

SUMMARY DATA OF TEST SP-2 (OWENS-ILLINOIS TYPE 650 RESIN, HEAT CURED)

| m/e | Probable Gas Species | Warm Polymer Background | Warm Polymer Background | Polymer under $LN_2$ only | Polymer under $LN_2$ + UV * | Warm Polymer Gas Bleed** |
|---|---|---|---|---|---|---|
| 2 | $H^+$ | 270 | 140 | 32 | 99 | 91 |
| 12 | $C^+$ | 13 | 2 | 9.6 | 8 | 6.3 |
| 13 | $CH^+$ | 2.3 | 0.3 | 0.9 | 0.7 | 0.7 |
| 14 | $CH_2^+, N^+$ | 13 | 2.4 | 6.8 | 64 | 7.2 |
| 15 | $CH_3^+$ | 23 | 3.4 | 5.3 | 4.8 | 5.5 |
| 16 | $CH_4^+, O^+$ | 35 | 5.1 | 14 | 13.3 | 12.6 |
| 17 | $OH^+, CH_5^+$ | 154 | 16 | 39 | 32.2 | 38 |
| 18 | $H_2O^+$ | 522 | 60 | 132 | 108 | 126 |
| 25 | $C_2H^+$ | Trace | | Trace | 0.2 | 0.2 |
| 26 | $C_2H_2^+$ | 3 | 0.8 | 1 | 1.1 | 1.2 |
| 27 | $C_2H_3^+$ | 8 | 1.8 | 2.5 | 2.6 | 2.2 |
| 28 | $C_2H_4^+, CO^+, N_2^+$ | 100 | 100 | 100 | 100 | 100 |
| 29 | $C_2H_5^+$ | 8 | 2.6 | 2.9 | 3 | 3.4 |
| 30 | $C_2H_6^+$ | 13 | 2.3 | 4.6 | 4 | 1.7 |
| 31 | | 19 | 1.1 | 0.5 | 0.5 | 3.4 |
| 32 | | 1 | 0.8 | 2.7 | 2.4 | 3.8 |
| 36 | $C_3^+$ | Trace | 0.3 | 0.7 | 0.7 | 0.3 |
| 39 | $C_3H_3^+$ | 2.3 | Trace*** | 0.4 | 0.7 | 0.3 |
| 40 | $C_2O^+, A^+$ | Trace | Trace | Trace | 0.4 | 0.5 |
| 41 | | 3.1 | 0.6 | 0.4 | 0.8 | 0.2 |
| 42 | | 1 | 0.3 | 0.4 | 0.6 | 0.2 |
| 43 | | 7 | 0.8 | 1.1 | 1.3 | 1 |
| 44 | $CO_2^+$ | 17 | 11.4 | 21.2 | 25 | 17 |
| 45 | | 1 | 0.6 | 0.4 | 0.5 | |
| 103 | | 0.8 | 0.4 | 1.4 | 1.4 | 0.7 |
| 201 | | 0.8 | 0.4 | 1.4 | 1.6 | 0.5 |

* $LN_2$ level dropped during irradiation

** Leaked in too fast

*** m/e 38.5 value was 0.6

significance is the increase in nitrogen and/or methane concentration on irradiation as evidenced by the ten-fold increase in m/e 14. The large initial background of m/e 18, which decreased during further pump-down, is indicative of moisture in the system -- probably from the glass-blowing operation when the ESR and mass spectra tubes were fused to the system. The mass peak at 201 is attributed to slight back-diffusion of mercury from the mercury diffusion pump.

Solid RTV-602 (catalyzed at 0.4% with SRC-05) was irradiated in test SP-3; the results are presented in Table 8. The hydrogen peak not only increased when the $LN_2$-cooled polymer was irradiated but increased still further when the polymer was warmed and the gases bled to the spectrometer. Methane peaks (12, 14, 15, 16 and 17 m/e) increased on irradiation and peaks at 14, 15 and 17 increased still futher when the gases trapped in the polymer were bled to the spectrometer. Water (18 m/e) appears to have been trapped in the irradiated, frozen polymer. An interesting observation is the increase in the m/e 29 peak, which could have been $C_2H_5^+$, when the irradiated polymer is warmed. Similarly, the m/e 39 peak ($C_3H_3^+$) increased when the polymer was warmed.

The Owens-Illinois Type 650 resin was irradiated a second time in test SP-4; the data are presented in Table 9. Although the hydrogen peak decreased on irradiation, considerable hydrogen was trapped in the frozen polymer. Little increase in m/e 12 through 16 was observed. The peak corresponding to m/e

Table 8

SUMMARY DATA OF TEST SP-3 (RTV-602/0.4% SRC05)

| m/e | Probable Gas Species | Clean/Dry Empty | Warm Polymer Background | Polymer under $LN_2$ only | Polymer under $LN_2$ + UV | Warm Polymer Gas Bleed |
|---|---|---|---|---|---|---|
| 2 | $H^+$ | 256 | 370 | 140 | 382 | 470 |
| 12 | $C^+$ | 28 | 5.8 | 5 | 10 | 0.3 |
| 13 | $CH^+$ | 2.3* | 1.8 | 2.5 | 4.2 | 4.7 |
| 14 | $CH_2^+, N^+$ | 28 | 9.7 | 7.5 | 12.5 | 14.9 |
| 15 | $CH_3^+$ | 18.6 | 23.6 | 25 | 35 | 59.3 |
| 16 | $CH_4^+, O^+$ | 22 | 18 | 28 | 35 | 14.4 |
| 17 | $OH^+, CH_5^+$ | 49 | 43 | 14 | 10 | 25 |
| 18 | $H_2O^+$ | 160 | 182 | 46 | 27.6 | 84 |
| 25 | $C_2H^+$ | Trace | 0.4 | Trace | 0.8 | 3 |
| 26 | $C_2H_2^+$ | 1.2 | 3.3 | 3 | 5 | 11 |
| 27 | $C_2H_3^+$ | 3 | 10.8 | 8 | 11.6 | 10 |
| 28 | $C_2H_4^+, CO^+, N_2^+$ | 100 | 100 | 100 | 100 | 100 |
| 29 | $C_2H_5^+$ | 3.5 | 5.1 | 3.5 | 4.2 | 54 |
| 30 | $C_2H_6^+$ | 25.6 | 12.2 | 5.0 | 4.2 | 5.8 |
| 31 | | 0.2 | 0.8 | Trace | Trace | 1 |
| 32 | | 2.1 | 0.4 | 1 | 2.1 | 1.2 |
| 36 | $C_3^+$ | 0.5 | Trace | Trace | Trace | 1 |
| 39 | $C_3H_3^+$ | 0.5 | 1.7 | 1 | 0.8 | 3.9 |
| 40 | $C_3O^+, A^+$ | 0.2 | 1.1 | 2.5 | 1.7 | 1.9 |
| 41 | | 0.7 | 2.5 | 2.5 | 2.5 | 1.9 |
| 42 | | 0.7 | 3.2 | 4 | 2.5 | 3.1 |
| 43 | | 3.7 | 6.2 | 3 | 2.5 | 36 |
| 44 | $CO_2^+$ | 41.8 | 16.7 | 17.5 | 10.8 | 8.1 |
| 45 | | 0.7 | 2.1 | 1.5 | 1.7 | 0.8 |
| 103 | | 2.1 | 0.4 | 1.5 | 0.8 | 0.8 |
| 201 | | 2.3 | 0.4 | 1.5 | 0.8 | 0.3 |

*m/e = 1.5 with value of 0.1

Table 9

SUMMARY DATA OF TEST SP-4 (OWENS-ILLINOIS TYPE 650 RESIN, HEAT CURED)

| m/e | Probable Gas Species | Warm Polymer Background | Polymer under $LN_2$ only | Polymer under $LN_2$ + UV | Polymer under $LN_2$ + UV | Warm Polymer Gas Bleed |
|---|---|---|---|---|---|---|
| 2 | $H^+$ | 2110 | 760 | 366 | 248 | 554 |
| 12 | $C^+$ | 10.8 | 5 | 4.8 | 13.5 | 13.4 |
| 13 | $CH^+$ | 6* | 1 | 2.6 | 3.4 | 3.5 |
| 14 | $CH_2^+, N^+$ | 23 | 12 | 8.6 | 11.1 | 10.2 |
| 15 | $CH_3^+$ | 53 | 15 | 29 | 20 | 26.8 |
| 16 | $CH_2^+, O^+$ | 44.5 | 16 | 29.5 | 27 | 23.2 |
| 17 | $OH^+, CH_5^+$ | 32.8 | 20 | 7.1 | 25.7 | 32 |
| 18 | $H_2O^+$ | 97.5 | 72 | 23.7 | 77 | 98 |
| 25 | $C_2H^+$ | 12 | Trace | 0.3 | 0.3 | 0.4 |
| 26 | $C_2H_2^+$ | 72 | 4 | 2 | 2.7 | 1.8 |
| 27 | $C_2H_3^+$ | 16.9 | 8 | 4 | 4.9 | 2.9 |
| 28 | $C_2H_4^+, CO^+, N_2^+$ | 100 | 100 | 100 | 100 | 100 |
| 29 | $C_2H_5^+$ | 16.4 | 5 | 5.7 | 3.4 | 14.7 |
| 30 | $C_2H_6^+$ | 4.8 | 2 | 1.1 | 2.7 | 2.9 |
| 31 | | 4.2 | 1 | 0.3 | 0.3 | 15.3 |
| 32 | | 3 | 3 | 0.9 | 2.7 | 8.9 |
| 36 | $C_3^+$ | Trace | 1 | 0.3 | 0.9 | Trace |
| 39 | $C_3H_3^+$ | 3.6 | 2 | 0.9 | 1 | 0.1 |
| 40 | $C_3O^+, A^+$ | | 1 | 0.3 | 0.6 | 0.3 |
| 41 | | 20 | 3 | 1 | 2 | 0.4 |
| 42 | | 3 | 1 | 0.6 | 0.4 | 0.3 |
| 43 | | Trace | 4 | 1.1 | 0.4 | 1.4 |
| 44 | $CO_2^+$ | 7.2 | 14 | 8.6 | 24 | 13 |
| 45 | | 1.2 | 1 | 0.3 | 1.6 | 1.0 |
| 55.5 | | 3.6 | 1 | Trace | 0.3 | Trace |
| 83 | | 1.8 | Trace | Trace | 1.9 | |
| 201 | | Trace | Trace | Trace | 0.6 | 0.4 |

*m/e = 13.5 value trace

17 ($OH^+$,$CH_5^+$) increased after an initial decrease during irradiation; the peak increased still further when the polymer was warmed. The peak for m/e 18 behaved similarly to that corresponding to m/e 17. Peaks corresponding to m/e 29 ($C_2H_5^+$) and m/e 31 exhibited significant increases when the frozen polymer was warmed. Traces of mercury contamination were again observed.

## C. Electron Spin Resonance Spectra

Four ultraviolet irradiated samples were studied during the past research period. Two of the above samples were further irradiated with $\gamma$-rays and the ESR spectra were obtained at 77°K. The appearance of the spectra is given below.

### 1. SP-1B (Oxidatively Crosslinked Polydimethylsiloxane

The spectrum presented in Figure 1 shows one strong central line and two weak satellite lines. The central line is asymmetric and it appears to be two lines superimposed on each other. The two weak satellite lines are wider than the central line and may consist of more than two lines. The g-factor of the central line is 2.000. The weak satellite lines are not completely resolved.

### 2. LP-4 (RTV-602)

The central line is highly asymmetric. The line width measured between points of inflection is approximately 4.5 gauss and it is similar to the spectrum shown in Figure 1. There appears to lie more than one weak line on each side of the strong central line. A more complete analysis of this

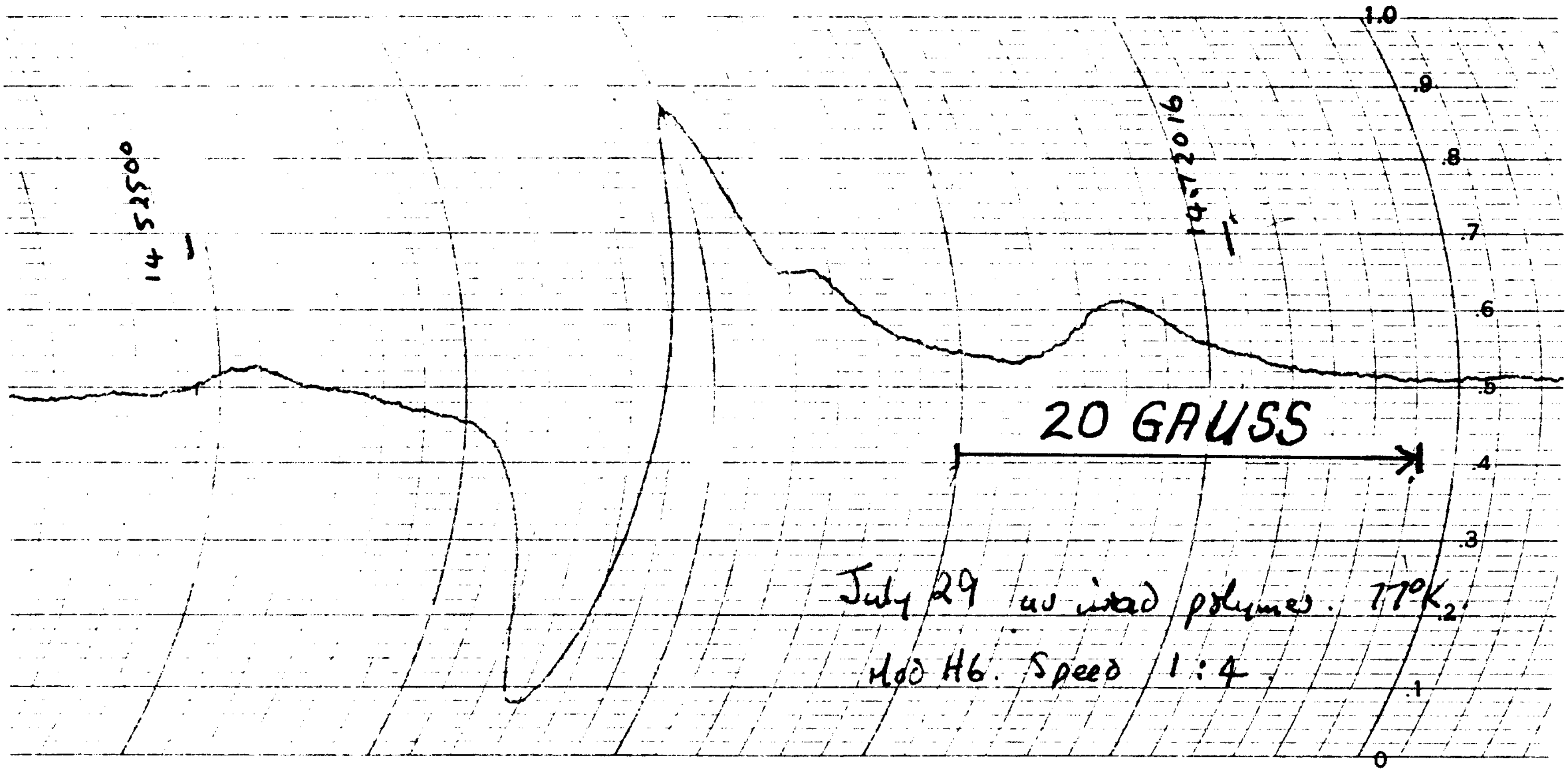


Figure 1

ESR SPECTRUM OF ULTRAVIOLET IRRADIATED OXIDATIVELY CROSSLINKED POLYDIMETHYLSILOXANE (SP-1B) spectrum, shown in Figure 2, is given in this report.

3. SP-2 (OI Type 650)

A fairly weak ESR spectrum was observed in this sample. Three lines similar to spectra #1 and #2 (SP-1B and LP-4) were observed. The central line is again highly asymmetric and the high field satellite line is unresolved. The spectra is presented in Figure 3. This spectrum is seen to be different from previous spectra because of the absence of the low field satellite line.

4. SP-3 (RTV-602/SRC-05)

A very weak ESR spectrum, shown in Figure 4, was observed in this sample. Only the central line appears definitely. The satellite lines observed in the previous samples are not clearly resolved.

5. Analysis of ESR Spectrum #2 (LP-4)

Figure 2 is a trace of the ESR spectrum of ultraviolet irradiated RTV-602 polydimethylsiloxane taken at 77°K immediately following the irradiation. It is noted that this spectrum is significantly different from that obtained in the initial investigation (see Analysis I) with the appearance of at least two other lines labeled $H_{x_1}$ and $H_{x_2}$ on the recorder tracing. This suggests the presence of three or more paramagnetic species, one associated with the components $H_y^1$, $H_y^2$ and $H_o$ (where $H_{y2} - H_{y1} = 35$ gauss) the second associated with $H_{x_1}$ and $H_{x_2}$ and the third associated with $H_{z_1}$, $H_o$ and $H_{z_2}$ (unresolved). The large asymmetry in the central line (labeled

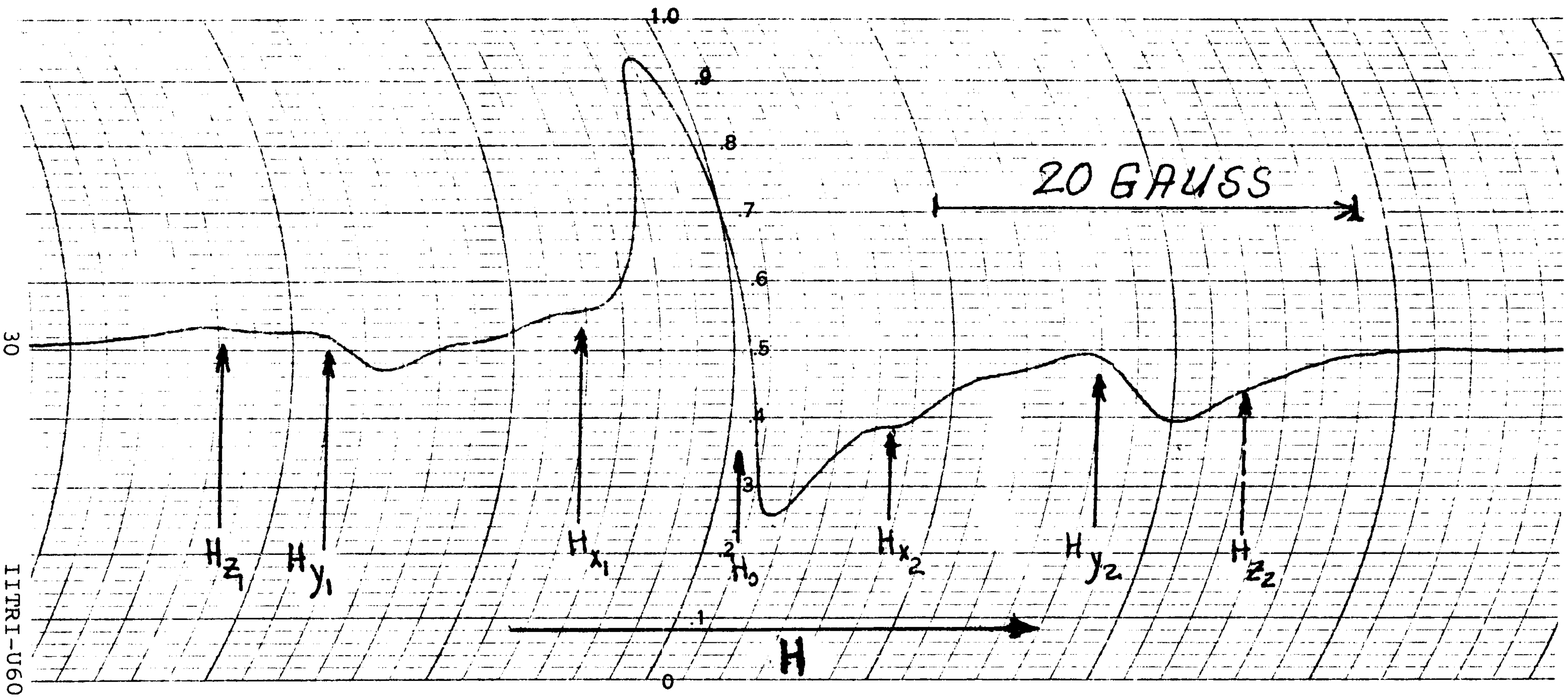


Figure 2

ESR SPECTRUM OF ULTRAVIOLET IRRADIATED RTV-602 (LP-4)

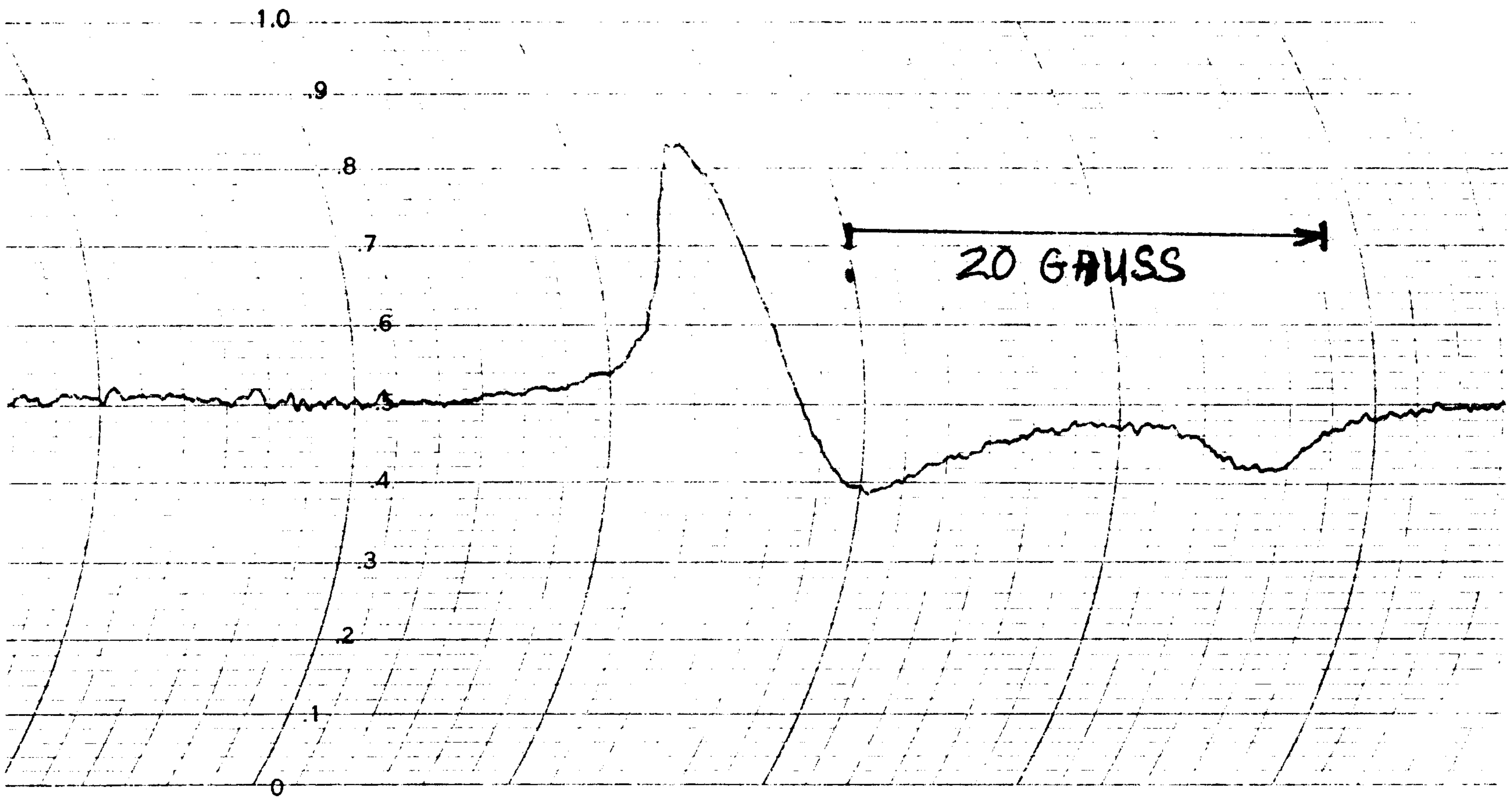


Figure 3

ESR SPECTRUM OF ULTRAVIOLET IRRADIATED OWENS-ILLINOIS
TYPE 650 SILICONE (SP-2)

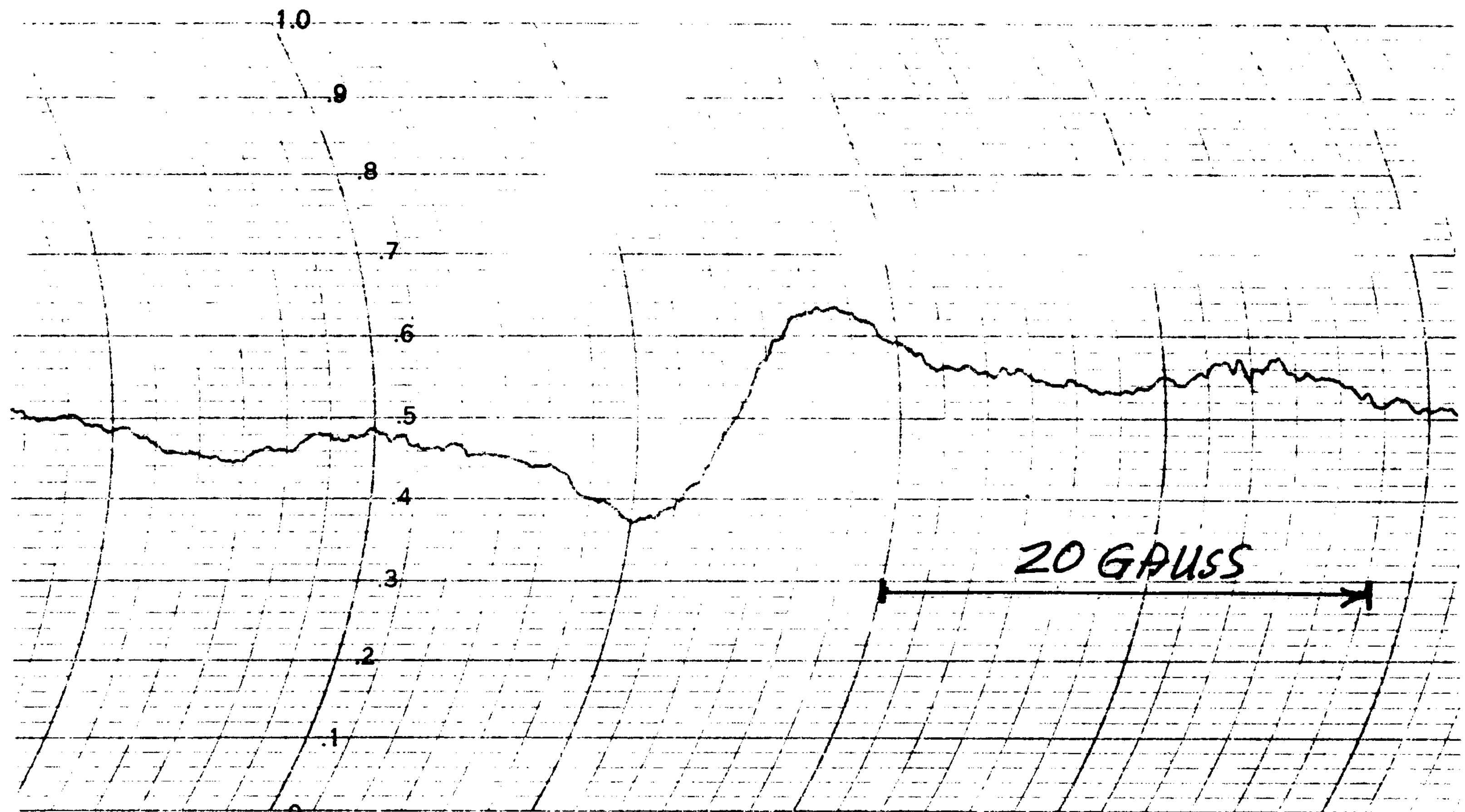


Fig. 4

Figure 4

ESR SPECTRUM OF ULTRAVIOLET IRRADIATED RTV-602
CURED WITH 0.4% SRC-05 CATALYST (SP-3)

$H_o$) is probably due to the superposition of two or more lines which are shifted by some small amount. If the radicals associated with the y and z species give triplet spectra then their central components would be shifted from one another to give the asymmetric line observed at $H_o$. Since the central component is stronger than the sum of the outer components of y and z there is most likely at least one singlet at this field position.

7. Gamma Irradiation of UV-Irradiated Samples

Two samples which had been previously irradiated with ultraviolet and warmed to 300°K were subsequently $\gamma$-irradiated at 77°K and their ESR spectral were obtained. In both cases, intense ESR spectra were observed as compared to the spectra obtained in the ultraviolet-irradiated samples. See Figures 5 and 6. In one case, a symmetric central line (spectrum #5) was observed, which appears as a narrow line superimposed on a wide line. The data of $\gamma$-irradiated polymer spectra are summarized in Table 10.

In one of the $\gamma$-irradiated polymers the ESR spectrum due to atomic hydrogen was observed. This spectrum appears as a well resolved doublet due to the hyperfine interaction of the unpaired electron with the hydrogen nucleus. The linewidths of the hydrogen lines are approximately 3 gauss. The hyperfine splitting calculated to first order is 505 grams. This compares very well to the hyperfine splitting for free atomic hydrogen measured in the gaseous state. It is questionable

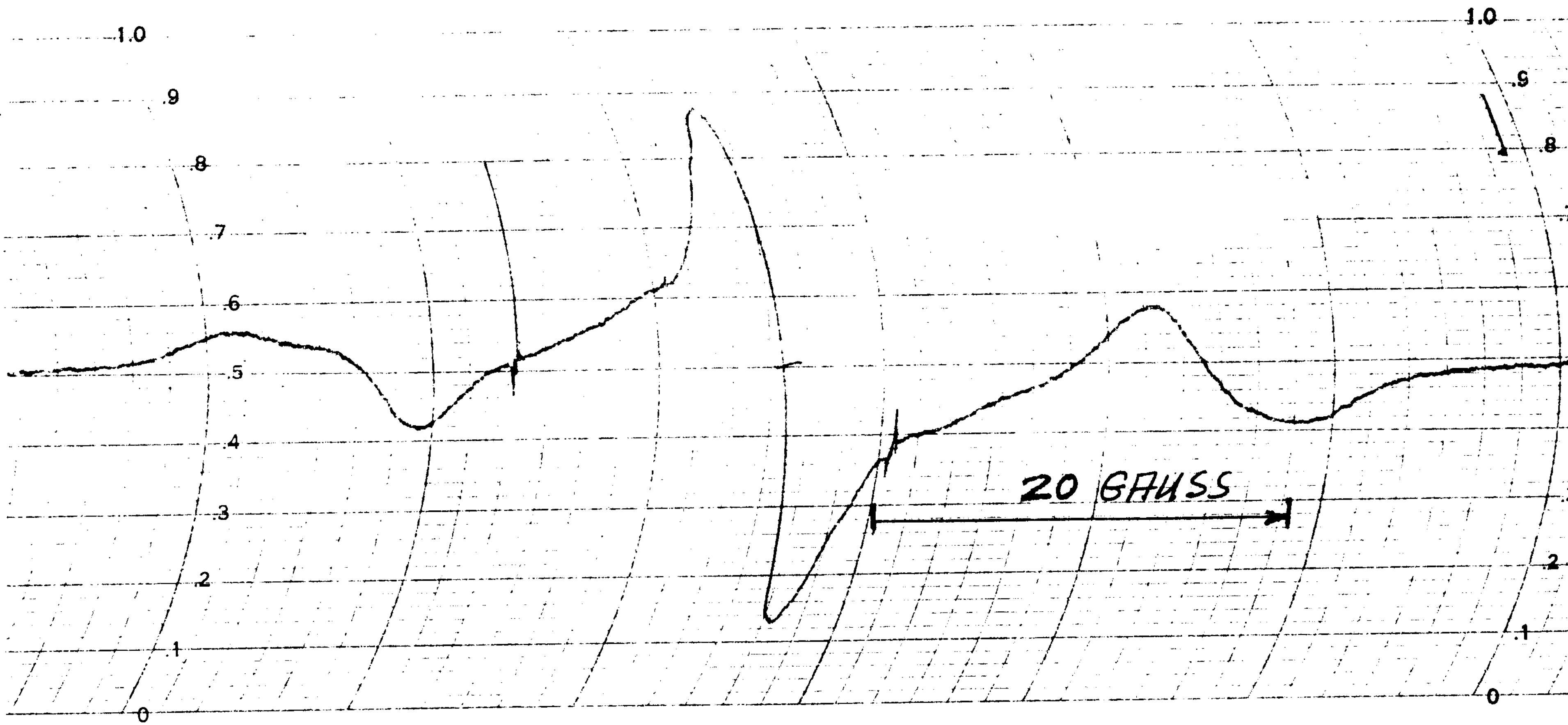


Figure 5

ESR SPECTRUM OF RTV-602 POLYDIMETHYLSILOXANE
(LP-4) $\gamma$-IRRADIATED AFTER DECAY OF UV-INDUCED ESR SPECTRUM

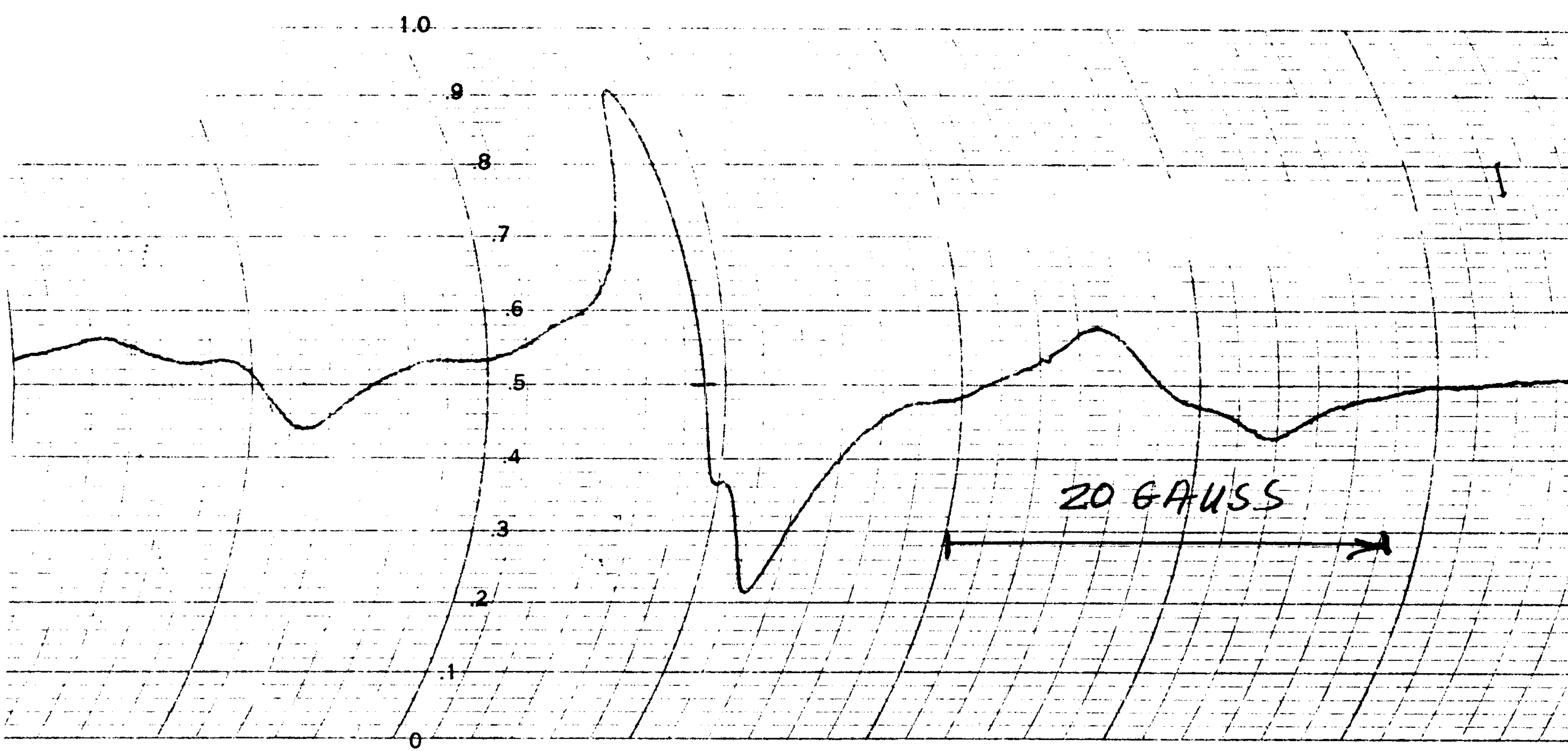


Figure 6

ESR SPECTRUM OF OXIDATIVELY CROSSLINKED POLYDIMETHYLSILOXANE (SP-1B) $\gamma$-IRRADIATED AFTER DECAY OF UV-INDUCED ESR SPECTRUM

Table 10

ESR SPECTRA OF $\gamma$-IRRADIATED POLYMERS*

| | Low Field Component | Central Line | High Field Component |
|---|---|---|---|
| | | Specimen #5 | |
| g-factor | 2.015 | 2.003 | 1.991 |
| $\delta$ (gauss) | -20.0 | 0.0 | +20.2 |
| $\Delta H$ (gauss) | 5 | 3.2 | 5 |
| Lineshape | Unresolved | Symmetric | Asymmetric or Unresolved |
| | | Specimen #6 | |
| g-factor | 2.015 | 2.003 | 1.991 |
| $\delta$* | -20.1 | 0.0 | +20.2 |
| $\Delta H$* | 5 | 5.0 | 5 |
| Lineshape | Unresolved | Asymmetric or Unresolved | Unresolved |

*$\delta$ is the field separation between satellite and central component.

*$\Delta H$ is the linewidth between points of maximum slope.

whether the hydrogen spectrum which was observed is due to the formation of atomic hydrogen in the polymer. There is a possibility that hydrogen is present in the quartz tube in the form of chemisorbed $H_2O$. This has been observed by other investigations, however, if this were the case it should have been observed in all $\gamma$-irradiated specimens.

More complete analyses of the spectra will be given in the future reports when more experimental data will be available.

D. Summary

To summarize, it may be noted that in all ultraviolet-irradiated polymers the ESR spectra disappear in several seconds upon warming the samples to room temperature. All lines seem to decay at the same rate, but this observation will be investigated further.

More detailed analyses of the mass spectra data will be made. A computor program may be required to accurately interpret the original composition of the products evolved as a result of ultraviolet irradiation. The examination of data presented does indicate, however, that both hydrogen and methyl radicals are evolved as a result of the photolysis reactions. Mass peaks corresponding to carbon dioxide liberation ($CO_2^+$, 44 m/e; $C^+$, 12 m/e) were not observed in the tests performed during this report period, presumably due to a cleaner, more leak-free system.

The fact that electron spin resonance spectra were not generated for the last three specimens is of great concern. Tests SP-4 through SP-6 were performed after the controlled leak was repaired. The leak was altered immediately after test SP-3 and involved changing an epoxy seal to a leak-free, glass-to-metal seal. The change permitted evacuation of the chamber to an order of magnitude lower pressure. The possibility that epoxy or other contamination could have enhanced the previously observed photolysis, thereby increasing the number of defects to a level required for ESR analysis, has interesting possibilities. In any case, it appears that subsequent irradiations will require considerably longer exposure times. A thorough check of the system has shown that all glass materials were neither coated nor fabricated of ultraviolet absorbing, materials. The lack of ESR spectra can not otherwise be explained at this time.

Future studies will be performed in conjunction with our new Hitachi RMU-6D mass spectrometer. The spectrometer is single focussing ($M/\Delta M = 2000$) and equipped with an electron-multiplier detector for high-sensitivity detection (fractions of a ppm). Compounds with molecular weights up to 1500 can be analyzed with unit resolution. Mass spectrograms are produced on an oscillographic recorder providing rapid recording at high scan rates (m/e of 12-500 in 3 sec.).

Additional ESR determinations are planned for specimens irradiated with $\gamma$-rays both prior to ultraviolet irradiation and after ultraviolet-induced ESR spectra have decayed. It is hoped that such tests will elucidate the reason for the lack of spectra in the last three polymers irradiated. In conclusion, it is noted that the absence of ESR spectra, coloration and physical-properties changes in these polymers is strongly indicative of an absence of damage.

## V. CONCLUSIONS

The most significant results of the work reported are listed in the following paragraphs.

Rutile, zirconia- and antimony oxide-opacified borosilicate porcelain coatings were found to possess exceptional stabilities. The $\Delta\alpha$ of only 0.03 in 2150 ESH exhibited by the antimony-pigmented porcelain is in direct contrast to the usual increase of >0.50 observed for silicate-bonded antimony oxide coatings after similar exposure. The rutile porcelain's initial solar absorptance was 0.25 and it exhibited a $\Delta\alpha$ of only 0.01. The zirconia porcelain possesses a $\Delta\alpha$ of -0.01. These observations tend to emphasize the importance of examining the influence of surface states on stability.

Doping of USP-12 zinc oxide with 0.01 and 0.1% lithium significantly improved the stability of zinc oxide powder at little cost to the initial solar absorptance. The $\Delta\alpha$ of USP-12 was 0.010 in 1760 ESH; the $\Delta\alpha$ of the 0.01% Li-doped specimen was 0.004 and that of the 0.10% Li-doped sample was 0.005.

An $\alpha$-alumina-pigmented Owens-Illinois Type 650 resin exhibited an initial solar absorptance of 0.09 and a $\Delta\alpha$ of 0.06 after 1700 ESH. The initial solar absorptance is the lowest ever obtained with a silicone vehicle. Better stability was achieved with a previous $\alpha$-alumina-silicone coating and this system will therefore be studied further.

Moisture appears to have little effect on the stability of S-13. An S-13 paint prepared under anhydrous conditions possessed a solar absorptance of only 0.15 for a 5-mil film, however. This is the most reflective S-13 specimen examined thus far.

A zinc oxide-pigmented Owens-Illinois Type 650 resin which was B-staged possessed improved physical properties and exhibited a $\Delta\alpha$ of only 0.002 after an exposure of 1700 ESH.

Photolysis studies during this period have shown that both hydrogen and methyl radicals are evolved during ultraviolet irradiation. Observations tend to reinforce the supposition that contamination plays a leading role in photolysis reactions in 100% methyl silicones.

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